

Comparison of Basis Set Superposition Error Corrected Perturbation Theories for Calculating Intermolecular Interaction Energies

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ABSTRACT: Recently, two different but conceptually similar basis set superposition error (BSSE) free second-order perturbation theoretical schemes were developed by us that are being based on the chemical Hamiltonian approach (CHA). Using these CHA-MP2 and CHA-PT2 methods, a comparison is made between the *a posteriori* and *a priori* BSSE correction schemes at the correlated level. Sample calculations are presented for four hydrogen bonded complexes ($\text{HF} \cdots \text{H}_3\text{N}$, $\text{HF} \cdots \text{H}_2\text{O}$, $\text{H}_2\text{S} \cdots \text{HF}$, and $\text{H}_2\text{O} \cdots \text{HCl}$) in nine different basis sets (from 6–31G to TZV**++). The results show that the BSSE content is very significant in the interaction energy if electron correlation is accounted for, so removing the BSSE is very important. The differences of the two perturbational theories discussed are connected solely with the different one electron orbital sets used for building up the unperturbed single determinant wave function. © 1999 John Wiley & Sons, Inc. *J Comput Chem* 20: 274–283, 1999

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Introduction

The problem of basis set superposition error (BSSE) in the theory of intermolecular interactions has been recognized for many years. Due to the use of finite basis sets, neither the energy of the whole interacting complex ("supermolecule") nor the energies of the individual constituting molecules ("monomers") are exact. When the interaction energy is calculated as the difference of these quantities, one observes a systematic imbalance that usually leads to too deep minima. This is connected with a better description of the *intra-monomer* energy when the extended basis of the whole complex becomes available. Several approaches have been proposed to account for this BSSE effect at the self-consistent field (SCF) and correlated levels of theory. These methods can be divided into approximately two groups. The first, most commonly used approach is the Boys–Bernardi (BB) counterpoise correction scheme¹ in which the supermolecule energy is used without any correction while the monomer energies are recomputed within the full dimer basis sets at any geometrical arrangement of the complex, so they become distance dependent.[†] In the other approach, one assumes that the free monomer energies are correct *for the given basis set*, and the BSSE has to be eliminated in some manner from the supermolecule calculation. Either one omits some terms from the supermolecule energy expression as being due to BSSE^{5,6} or one tries to get rid of it when determining the wave function as in the so-called chemical Hamiltonian approach (CHA).

In the CHA scheme (first introduced in ref. 7) one identifies and omits those terms of the Hamiltonian that are responsible for the BSSE. In this manner an efficient *a priori* BSSE correction method was constructed. Because BSSE is not a physical quantity, the "remaining" CHA Hamiltonian is not Hermitian. In solving this non-trivial problem (using the method of momenta instead of variational principle) SCF-type equations were derived to calculate BSSE-free wave functions.⁸ (Slightly different CHA-SCF equation giving practically the same results obtained by applying an analogous

treatment directly to the Fockian.^{9,10}) The numerical calculations and the analytical considerations both indicated that the energy should be calculated as a conventional expectation value of the original Born–Oppenheimer Hamiltonian and not of the "chemical one."^{10–12} (This is indicated by the expression "CHA with conventional energy," CHA/CE.)

Several comparative studies were performed at the SCF level^{2,9}, and they showed that for not too small basis sets the CHA and BB results are usually very close to each other. For medium-size bases some "overcorrecting" behavior of the BB scheme can usually be observed, leading to curves with slightly too shallow minima that are also somewhat shifted to larger intermolecular separations. It was also found that the difference between the *a posteriori* BB and the *a priori* CHA curves diminishes much faster when the basis set increases than when the BSSE vanishes from the uncorrected SCF results.

Electron correlation plays a very important role for the intermolecular interactions in the hydrogen bonded and van der Waals systems,^{13–15} and its accurate treatment is essential. For large enough basis sets, BSSE effects at the Hartree–Fock level are much smaller than those at the correlated level. In practice, one can closely approach the basis set limit of the SCF interaction energy by using basis sets for which the BSSE content of the correlation energy is still very large and is comparable to the actual value of the intermolecular interaction energy. (At the same time, the use of much larger basis sets might be affordable for SCF but not for correlated calculations.) So, it is very important to deal properly with the BSSE problem at the correlated level and many different approaches have been developed to account for them.^{13–15} Several attempts have also been made by using the CHA philosophy to find an appropriate simultaneous treatment of electron correlation and the BSSE problem.^{16–22} [These include the development of the CHA-density functional theory (DFT), too.^{20–22}] The pivot four-electron full configuration interaction calculations¹⁷ showed that the CHA scheme should also be applicable at the electron correlated level of theory. At present, two different types of second-order perturbation theories (CHA-MP2, CHA-PT2) are available for practical applications.

In the present work our aim is to give a short summary of the CHA-MP2 and CHA-PT2 methods^{18,19} and to extend our previous comparative studies on hydrogen bonded systems.^{2,9,23} To as-

[†]One can show^{2,3} that this treatment involves a tacit assumption about the *additivity* of the BSSE effects. Also, this scheme encounters a special difficulty if one wishes to take into account the change of the monomer geometries during the complex formation.⁴

sess the possibilities of the *a priori* BSSE-free CHA scheme at the electron correlation level, we compare the two versions of the CHA-based second-order PT with the *a posteriori* BSSE-corrected MP2/BB method.

CHA-PT2 and CHA-MP2 Schemes

Both theories start from the same second-order BSSE-free intermolecular energy formula,

$$E^{(2)} = \frac{\langle \Psi_0 | \hat{H} | \Psi_0 \rangle}{\langle \Psi_0 | \Psi_0 \rangle} + J_2, \quad (1)$$

but differ in the definition of the different operators and wave functions entering it. The first term in the right-hand side of (1) is the expectation value of the total Hamiltonian over the unperturbed wave function. The second term in (1) is the Hylleraas functional, representing the second-order BSSE-free energy contribution. In both theories the unperturbed Hamiltonian is non-Hermitian; the expression for the J_2 functional for such a case is given in ref. 24.

$$J_2 = \frac{1}{\langle \Psi_0 | \Psi_0 \rangle} \left[\langle \chi | \hat{V} - E_1 | \Psi_0 \rangle + \langle \Psi_0 | \hat{V}^\dagger - E_1^* | \chi \rangle + \text{Re}(\langle \chi | \hat{H}_0 - E_0 | \chi \rangle) \right]. \quad (2)$$

In these formulas Ψ_0 and E_0 are the zero-order ground state wave function and energy, respectively; \hat{V} is the perturbation operator; and $|\chi\rangle$ is the first-order wave function. As usual, E_1 is defined as $E_1 = \langle \Psi_0 | \hat{V} | \Psi_0 \rangle$. It is easy to see that for Hermitian \hat{H}_0 and \hat{V} and for normalized Ψ_0 (2) trivially reduces to the usual second-order Hylleraas functional.]

MONOMER-BASED CHA-PT2 THEORY

In the CHA-PT2 scheme one starts from the orbitals and orbital energies of the unperturbed free monomers. We define the zero-order effective one-electron Hamiltonian as the sum of the “effective” monomer Hartree–Fock operators,

$$\hat{H}_0 = \hat{F}_A + \hat{F}_B, \quad (3)$$

where

$$\hat{F}_A = \sum_{i \in A} \varepsilon_i \hat{i}^+ \hat{i}^- \quad \text{and} \quad \hat{F}_B = \sum_{i \in B} \varepsilon_i \hat{i}^+ \hat{i}^-, \quad (4)$$

with ε_i being the respective orbital energies, and \hat{i}^+ and \hat{i}^- are the creation and “effective” annihilation operators²⁵ corresponding to the monomer MO-s φ_i . The unperturbed ground state wave function is chosen as the antisymmetrized product of the monomer ground state wave functions:

$$|\Psi_0\rangle = \hat{i}_{A_1}^+ \hat{i}_{A_2}^+ \cdots \hat{i}_{A_n}^+ \hat{i}_{B_1}^+ \cdots \hat{i}_{B_m}^+ |\text{vac}\rangle, \quad (5)$$

where n and m are the number of electrons on molecules A and B . The perturbation can be written as

$$\hat{V}_{\text{CHA}} = \hat{H}_{\text{CHA}} - \hat{H}_0. \quad (6)$$

In this theory the first term on the right-hand side of (1) may be called the Heitler–London energy that corresponds to the wave function obtained by simple antisymmetrization of the unperturbed monomer wave functions; it can be most conveniently calculated by performing an orthogonalization of the original occupied monomer orbitals in the supermolecule basis. Using the CHA Hamiltonian⁷ and a biorthogonal formalism (e.g., ref. 25), an explicit expression for the first-order wave function was obtained¹⁸:

$$\begin{aligned} |\chi\rangle = & -\frac{1}{4} \sum_{i,j \in A}^{\text{occ}} \sum_{p,q \in A}^{\text{virt}} \frac{[pq||ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j} |\Psi_{ij}^{pq}\rangle \\ & - \sum_{i \in A}^{\text{occ}} \sum_p^{\text{virt}} \frac{\langle \tilde{p} | \hat{V}_B^{\text{aux}} | i \rangle}{\varepsilon_p - \varepsilon_i} |\Psi_i^p\rangle \\ & - \frac{1}{4} \sum_{i \in A}^{\text{occ}} \sum_{j \in B}^{\text{occ}} \sum_{p,q}^{\text{virt}} \frac{[\tilde{p}q||ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j} |\Psi_{ij}^{pq}\rangle \\ & + (A \leftrightarrow B). \end{aligned} \quad (7)$$

Here the notation $(A \leftrightarrow B)$ means that all terms with A and B interchanged should be added. The auxiliary operator \hat{V}_B^{aux} is defined through its matrix elements as

$$\langle \tilde{p} | \hat{V}_B^{\text{aux}} | i \rangle = \langle \tilde{p} | \sum_{a \in B} \frac{-Z_a}{r_a} | i \rangle + \sum_{j \in B}^{\text{occ}} [\tilde{p}j||ij]. \quad (8)$$

Here \tilde{p} and \tilde{j} refer to the biorthogonal counterparts of the monomer spin orbitals φ_p and φ_j , respectively ($\langle \tilde{\psi}_p | \varphi_i \rangle = \delta_{ip}$, etc.). The first term on the right-hand side of (7) describes intramonomer correlation and it contains integrals over the original spin orbitals only (i.e., no biorthogonal orbitals occur in it); this is the consequence of BSSE terms being eliminated from the CHA Hamiltonian. All terms of this sum coincide with the respective ones

in the first-order wave functions describing the intramonomer correlation in the free monomers; the monomer correlation energies, however, are not *strictly* recovered when wave function (7) is used due to the nonorthogonality.

The molecular orbitals φ_i and φ_j centered on different monomers are generally nonorthogonal. In order to calculate the matrix elements in the expression of J_2 , an auxiliary orthonormalized set of spin orbitals $\{\vartheta_i\}$ was introduced. These orbitals span the same space as the original ones $\{\varphi_i\}$ and are defined in such a manner that first the occupied orbitals of both monomers are orthonormalized among others and then the virtual orbitals are orthogonalized to the occupied subspace:

$$\varphi_p = \sum_l K_{lp} \vartheta_l, \quad (9)$$

$$\vartheta_p = \sum_l (\mathbf{K}^{-1})_{lp} \varphi_l. \quad (10)$$

\mathbf{K} is the transformation matrix of this orthogonalization. Using the above prescription, after a somewhat lengthy derivation an explicit expression can be obtained for J_2 in terms of the *spatial monomer orbitals*:

$$\begin{aligned} J_2 = & 2 \sum_k^{\text{occ}} \left\{ a(k|k) + \sum_{l < k}^{\text{occ}} [2u(kl|kl) - u(kl|lk)] \right\} \\ & \times 2 \sum_k^{\text{occ}} \left\{ d(k|k) + \sum_{l < k}^{\text{occ}} [2v(kl|kl) - v(kl|lk)] \right\} \\ & + 4 \sum_k^{\text{occ}} \sum_t^{\text{virt}} \left\{ \left[a(t|k) + \sum_l^{\text{occ}} (2u(tl|kl) - u(tl|lk)) \right] \right. \\ & \times \left[2 \langle \vartheta_t | \hat{h} | \vartheta_k \rangle + d(t|k) \right. \\ & \left. \left. + \sum_l^{\text{occ}} (2v(tl|kl) - v(tl|lk)) \right] \right\} \\ & + 4 \sum_{k < l}^{\text{occ}} \sum_{t < r}^{\text{virt}} \{ [2u(tr|kl) - u(tr|lk)] \\ & \times [4[\vartheta_t \vartheta_r | \vartheta_k \vartheta_l] - 2[\vartheta_t \vartheta_r | \vartheta_l \vartheta_k] \\ & + 2v(tr|kl) - v(tr|lk)] \}, \quad (11) \end{aligned}$$

where the different auxiliary quantities are defined as follows:

$$a(t|k) = \sum_{i \in A}^{\text{occ}} \sum_p^{\text{virt}} K_{tp} \frac{-\langle \tilde{p} | \hat{V}_B^{\text{aux}} | i \rangle}{\varepsilon_p - \varepsilon_i} K_{ik}^{-1} + (A \Leftrightarrow B), \quad (12)$$

$$d(t|k) = \sum_{i \in A}^{\text{occ}} \sum_p^{\text{virt}} -K_{tp} \langle \tilde{p} | \hat{V}_B^{\text{aux}} | i \rangle K_{ik}^{-1} + (A \Leftrightarrow B), \quad (13)$$

$$u(tr|kl) = b(tr|kl) + c(tr|kl), \quad (14)$$

$$v(tr|kl) = e(tr|kl) + f(tr|kl), \quad (15)$$

with

$$b(tr|kl) = \sum_{i, j \in A}^{\text{occ}} \sum_{p, q \in A}^{\text{virt}} K_{tp} K_{rq} \frac{-[pq|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j} \cdot K_{jl}^{-1} K_{ik}^{-1} + (A \Rightarrow B), \quad (16)$$

$$c(tr|kl) = \sum_{i \in A}^{\text{occ}} \sum_{j \in B}^{\text{occ}} \sum_{p, q}^{\text{virt}} K_{tp} K_{rq} \frac{-[\tilde{p}\tilde{q}|ij]}{\varepsilon_p + \varepsilon_q - \varepsilon_i - \varepsilon_j} \cdot K_{jl}^{-1} K_{ik}^{-1} + (A \Leftrightarrow B), \quad (17)$$

$$e(tr|kl) = \sum_{i, j \in A}^{\text{occ}} \sum_{p, q \in A}^{\text{virt}} -K_{tp} K_{rq} [pq|ij] K_{jl}^{-1} K_{ik}^{-1} + (A \Rightarrow B), \quad (18)$$

$$f(tr|kl) = \sum_{i \in A}^{\text{occ}} \sum_{j \in B}^{\text{occ}} \sum_{p, q}^{\text{virt}} -K_{tp} K_{rq} [\tilde{p}\tilde{q}|ij] K_{jl}^{-1} K_{ik}^{-1} + (A \Leftrightarrow B). \quad (19)$$

These expressions define our working formula²³ for the CHA-PT2 calculations. [The notations $A \Leftrightarrow B$ ($A \Rightarrow B$) indicate that the terms with A interchanged (replaced) with B should be added to the respective expression.]

SUPERMOLECULE CHA-MP2 THEORY

In the CHA-MP2 method one starts again from the CHA Hamiltonian.⁷ Solving the BSSE-free CHA-SCF equations, the zero-order unperturbed Hamiltonian can be chosen as

$$\hat{H}_0 = \sum_i \varepsilon_i \hat{i}^+ \hat{i}^-, \quad (20)$$

where \hat{i}^+ and \hat{i}^- are the creation and “effective” annihilation operators corresponding to the non-orthogonal (occupied and virtual) CHA canonic molecular orbital and ε_i is the respective eigenvalue of the CHA-SCF equations. To calculate the first-order wave function one again introduces an appropriate biorthogonal basis set defined by the left eigenvectors of the CHA Fockian. Then the perturbation may again be defined as

$$\hat{V}_{\text{CHA}} = \hat{H}_{\text{CHA}} - \hat{H}_0. \quad (21)$$

Only the orbitals and orbital energies on which \hat{H}_0 is built up differ from the previous case. One has to emphasize again that this \hat{H}_0 is not Hermitian. Because the orbitals used are a solution of the CHA-SCF equations, an analogue of the Brillouin theorem holds and the first-order wave function contains no singly excited configurations, only doubly excited ones:

$$|\Psi_1\rangle = - \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{virt}} \frac{\{\tilde{a}\tilde{b}||ij\}}{\varepsilon_a - \varepsilon_b - \varepsilon_i - \varepsilon_j} |\Psi_{ij}^{ab}\rangle. \quad (22)$$

Here the notation $\{\tilde{a}\tilde{b}||ij\}$ denotes the "CHA transformed" counterpart of the integral $[\tilde{a}\tilde{b}||ij]$ that can be obtained by the technique described in refs. 17 and 19.

Using the orthonormalized auxiliary spin orbitals $\{\vartheta_i\}$ defined in a manner similar to that discussed above, one can again derive the formula for J_2 :

$$J_2 = \text{Re} \left\{ \sum_{k,l}^{\text{occ}} t(kl||kl) \sum_{i,j}^{\text{occ}} y(ij||ij) + \sum_r^{\text{virt}} \sum_k^{\text{occ}} \left[\sum_l^{\text{occ}} t(lr||lk) \sum_j^{\text{occ}} y(jr||jk) - 2\langle \vartheta_r | \hat{F} | \vartheta_k \rangle \right] - \sum_{k < l}^{\text{occ}} \sum_{p < q}^{\text{virt}} t(pq||kl) [2[pq||kl] - y(pq||kl)] \right\}, \quad (23)$$

where the coefficients $t(pq||kl)$ and $y(pq||kl)$ are defined as

$$t(pq||kl) = \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{virt}} K_{pa} K_{qb} \frac{\{\tilde{a}\tilde{b}||ij\}}{\varepsilon_a + \varepsilon_b - \varepsilon_i - \varepsilon_j} K_{ik}^{-1} K_{jl}^{-1}, \quad (24)$$

$$y(pq||kl) = \sum_{i,j}^{\text{occ}} \sum_{a,b}^{\text{virt}} K_{pa} K_{qb} \{\tilde{a}\tilde{b}||ij\} K_{ik}^{-1} K_{jl}^{-1}. \quad (25)$$

Despite the seemingly simpler PT expressions, this formalism has two practical difficulties: first, its application requires the CHA-SCF equations to be solved at every point, which is a straightforward but relatively complex and costly procedure[‡]; second, its use is made more complicated by the possibility that the eigenvalues of the non-Hermi-

[‡]For use with CHA-MP2 one has to solve the more complicated "original" CHA-SCF equations (usually denoted CHA/CE^{9,12}) and not the much simpler heuristic CHA/F ones,^{2,10} because the Brillouin-type theorem does not strictly hold for the latter.

tian CHA Fockian can be complex. (A number of such cases has actually been encountered.) The resulting value of the second-order energy contribution is always real automatically, but the presence of the complex orbital energies either requires the use of complex computer arithmetics that reduce the effectivity considerably or rewriting the formulas in a manner that separately collects those terms the imaginary parts of which cancel in the final expression. However, this makes the theory significantly more difficult to handle.¹⁹

Computational Details

The computations were carried out on an IBM RS6000 and SGI Power Challenge workstations.

In calculations the HONDO-8 *ab initio* package of computer codes was utilized.²⁶ Standard MP2 and the BB-corrected MP2 calculations were performed by a slightly modified version of HONDO-8. The CHA-PT2 and CHA-MP2 calculations were done by codes written by us; they also utilized the one and two electron integrals produced by HONDO-8.

We considered all of the 25 different hydrogen bonds formed by the five molecules HCl, HF, NH₃, H₂O and H₂S, which can be obtained if each molecule is considered in the role of the hydrogen donor or the hydrogen acceptor. Because the curves often look similar, only four systems (HF · H₃N, HF · H₂O, H₂S · HF and H₂O · HCl) will be explicitly discussed: they represent the different cases ranging from weak interaction to strong ones. We used the same nine different basis sets (from 6-31G to TZV**+) as in ref 2 and simplified geometries as reported in ref. 27. During the studies of these systems, the intermolecular distance *R* was varied in a wide range, keeping fixed the internal geometry and the relative orientation of the monomers. These simplifications seemed reasonable because we are interested in a comparison of the different methods and not in the fine details of the structure of the actual systems.

During the examination Pople's 6-31G, Dunning's valence double zeta (DZV) and valence triple zeta (TZV) basis sets were used because they are generated by HONDO-8. In the polarized basis sets (denoted **) the exponents were different for each of the above-mentioned three basis sets. There are no standard exponents provided by HONDO-8 for the 6-31G** basis, so the following ones were taken from the Gaussian 92 system²⁸: hydrogen (*p*

orbitals): 1.1; oxygen, fluorine, sulfur, nitrogen, and chlorine ($6d$ orbitals): 0.8, 0.8, 0.65, 0.8, and 0.65, respectively. For the DZV** and TZV** basis, the following exponents were provided by HONDO-8: hydrogen (p orbitals): 1.0; oxygen, fluorine, sulfur, nitrogen, and chlorine ($6d$ orbitals for DZV): 0.85, 0.9, 0.6, 0.8, and 0.65, respectively: oxygen, fluorine, sulfur, nitrogen, and chlorine ($6d$ orbitals for TZV): 1.28, 1.62, 0.542, 0.98, and 0.619, respectively. The diffuse function (denoted by ++) had the following exponents: hydrogen (s orbitals): 0.036; oxygen, fluorine, sulfur, nitrogen, and chlorine (sp orbitals): 0.0845, 0.1076, 0.0405, 0.0845, and 0.0405, respectively.

Results and Discussion

The results for the four hydrogen bonded systems selected are presented in Figures 1–4. Con-

cerning the comparison of the results obtained with the uncorrected (MP2) and corrected (CHA-PT2, CHA-MP2, and MP2/BB) perturbational methods (Figs. 1–4), the following general remarks are appropriate: the amount of the BSSE content in the uncorrected energy is very large in all cases considered. Furthermore, in most cases the counterpoise (CP) corrected (MP2/BB) results are close to those given by the CHA-based perturbation theories. This is especially the case for the CHA-MP2 method utilizing the supermolecule CHA-SCF orbitals.

Considering the CHA-PT2 scheme, it may be noted that the minima obtained with this method are situated usually slightly above the CHA-MP2 and the MP2/BB ones, which is in contrast to the general observation that at different levels of the theory the CHA curves usually lie somewhat below the CP corrected ones. This effect is often not very evident; we selected the system $\text{H}_2\text{S} \cdots \text{HF}$ to

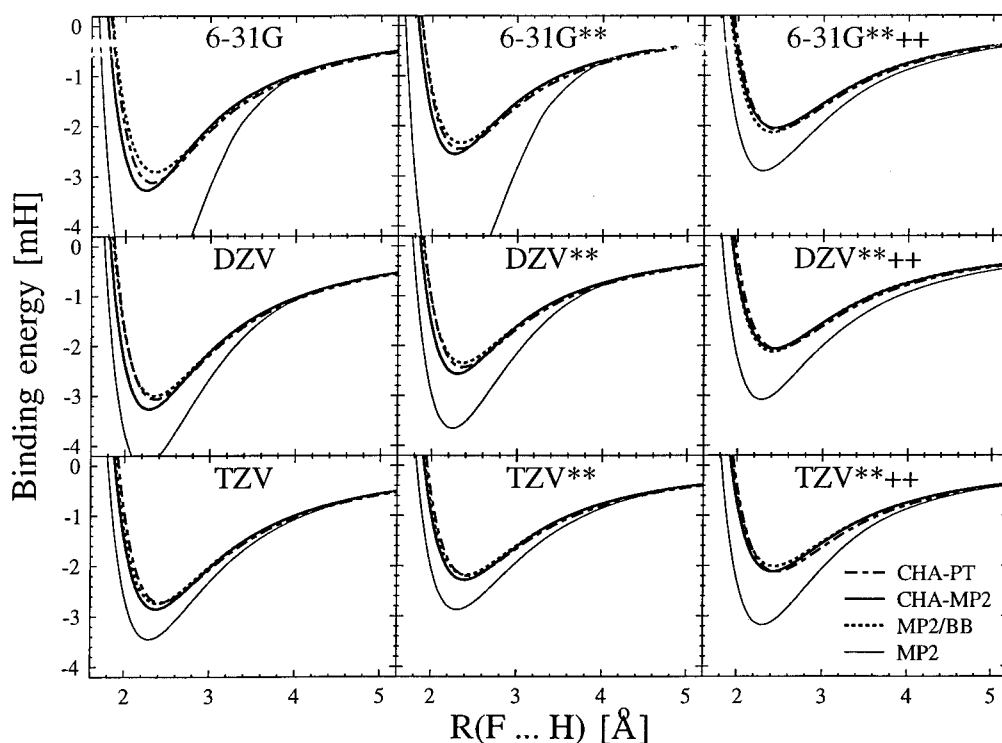


FIGURE 1. Potential curves of the $\text{HF} \cdots \text{H}_3\text{N}$ system calculated in nine different basis sets as a function of the hydrogen bond length. The coordinates (\AA) are $\text{H}_A(-0.38758; +0.83117; 0.0)$, $\text{F}_A(0.0; 0.0; 0.0)$, $\text{H}_B(R; 0.0; 0.0)$, $\text{N}_B(R + 1.0116; 0.0; 0.0)$, $\text{H}_{B_2}(R + 1.30229; -0.52927; -0.8116)$, and $\text{H}_{B_3}(R + 1.30229; -0.52927; +0.8116)$. The curves illustrate four different approximations to the interaction energy: MP2, standard uncorrected second-order perturbation theory; MP2 / BB, counterpoise corrected MP2 method; and CHA-PT2 and CHA-MP2, *a priori* BSSE-free second-order perturbation methods based on the chemical Hamiltonian approach.

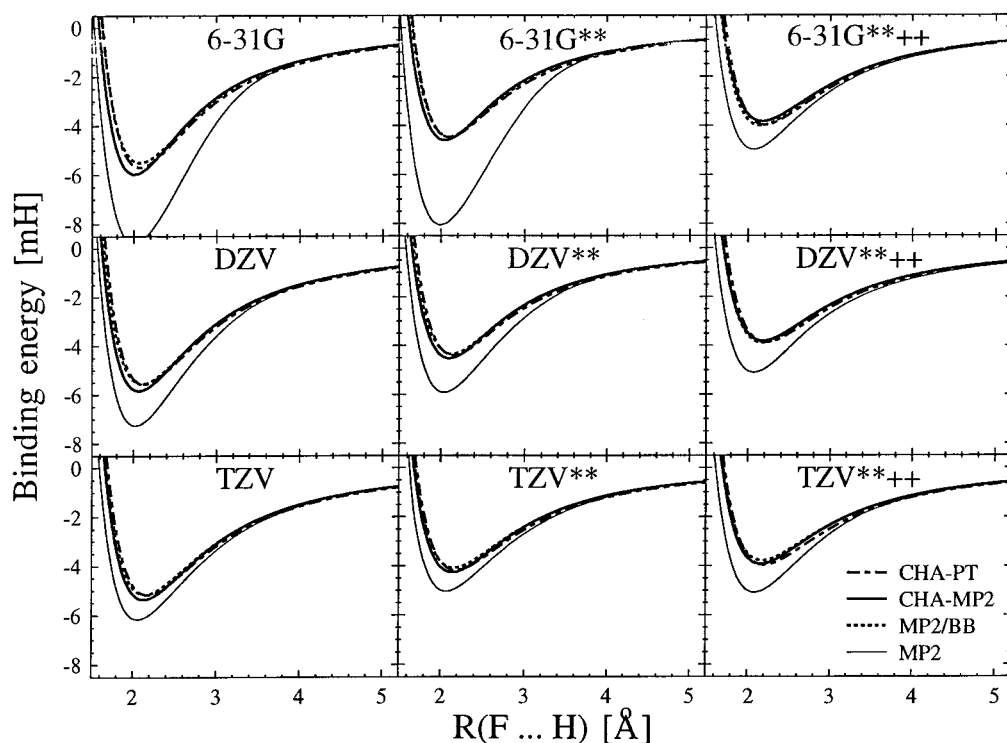


FIGURE 2. Potential curves of the $\text{HF} \cdot \text{H}_2\text{O}$ system calculated in nine different basis sets as a function of the hydrogen bond length. The coordinates (\AA) are $\text{H}_A(-0.45855; +0.79423; 0.0)$, $\text{F}_A(0.0; 0.0; 0.0)$, $\text{H}_{B_1}(R; 0.0; 0.0)$, $\text{O}_B(R + 0.957; 0.0; 0.0)$, and $\text{H}_{B_2}(R + 1.1966; -0.9265; 0.0)$. The notation of the individual curves is the same as for Figure 1.

show the case when it is the most pronounced. This behavior of the CHA-PT method is a consequence of the fact that in this theory the unperturbed Hamiltonian was chosen as the sum of the monomer Fockians, so that polarization and delocalization effects are taken into account up to second order only while these effects appear up to infinite order in the converged supermolecule calculations.

After having discussed the results in general, we have to emphasize that these complexes represent very different hydrogen bonded systems ranging from the weak bonding to the strong one. The electron correlation effect plays a decisive role for the true van der Waals systems (like rare gas dimers) that are not bonded at the SCF level of theory, while its importance is less for the hydrogen bonded systems discussed here. Obviously, their role is larger in the weakly bonded situations (see ref. 19 for an elaborated example) while in the strongly bonded complexes the electrostatic and

charge transfer effects dominate. As can be seen from the figures, the BSSE content of the results obtained by the 6-31G and 6-31G** basis sets is extremely large for $\text{HF} \cdot \text{H}_3\text{N}$ and $\text{HF} \cdot \text{H}_2\text{O}$, but it is much smaller with the better basis sets (Figs. 1, 2). An interesting, but not unusual, observation can be made by inspecting the curves (Figs. 3, 4) for $\text{H}_2\text{S} \cdot \text{HF}$ and $\text{H}_2\text{O} \cdot \text{HCl}$; the better basis sets exhibit larger BSSE. (The same holds for the TZV^{**++} basis in the case of $\text{HF} \cdot \text{H}_3\text{N}$.) This is connected with the known maximum character of BSSE: for small basis sets there is no flexibility for BSSE-caused energy lowerings, then BSSE increases and is reduced only after the saturation starts.[§]

An interesting difference can be observed between the behavior of the two PT schemes in the asymptotic region of large intermolecular separations. Although, of course, both schemes give po-

[§]At the SCF level the saturation occurs at much smaller basis sets than in the correlated case.

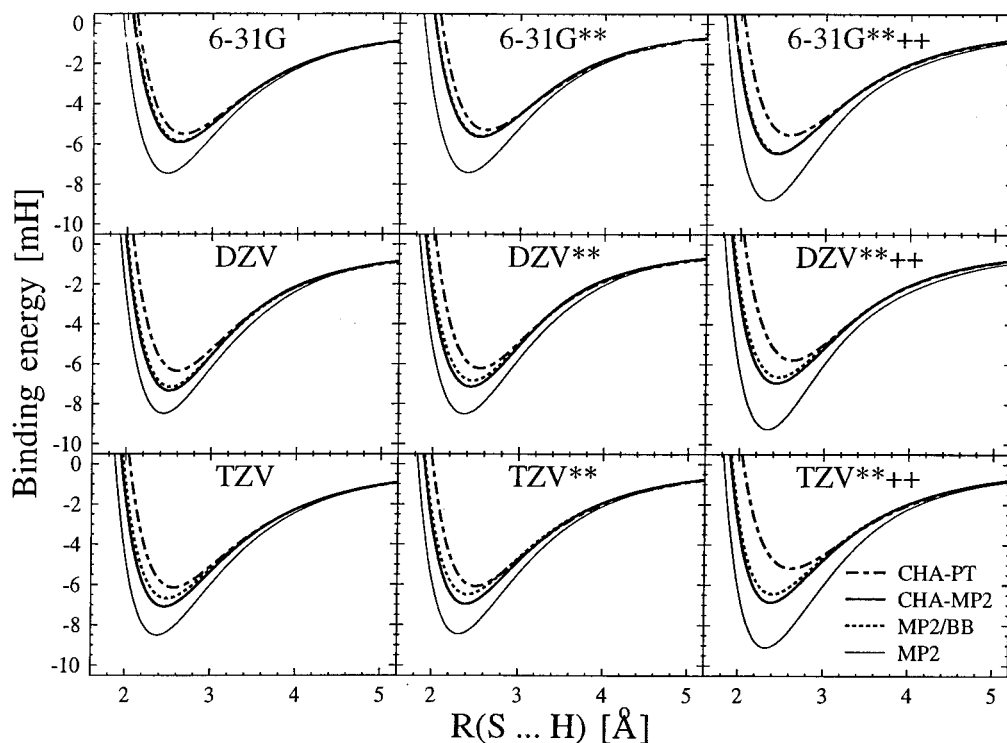


FIGURE 3. Potential curves of the $\text{H}_2\text{S} \cdots \text{HF}$ system calculated in nine different basis sets as a function of the hydrogen bond length. The coordinates (Å) are $\text{H}_{\text{A}_1}(-0.34503; +0.85397; -0.9571)$, $\text{H}_{\text{A}_2}(-0.34503; +0.85397; +0.9571)$, $\text{S}_{\text{A}}(0.0; 0.0; 0.0)$, $\text{H}_{\text{B}}(R; 0.0; 0.0)$, and $\text{F}_{\text{B}}(R + 0.9171; 0.0; 0.0)$. The notation of the individual curves is the same as for Figure 1.

tential curves that are very close to each other and tend to zero in the limit of the infinite distances, there is a general tendency that the CHA-MP2 curves systematically correspond to slightly higher energies than the CHA-PT2 ones. Moreover, at large distances the CHA-MP2 results (and similarly the MP2/BB ones) are above even of the CHA-SCF (and SCF/BB) data. This indicates that the correlation contribution to the interaction energy is *repulsive* at large distances. (This is, in fact, not a BSSE problem, because the same tendency can also be seen for the asymptotics of the uncorrected MP2 and SCF energies at such large distances where BSSE is already negligible.) At the same time the CHA-PT2 results are always below the BSSE-corrected SCF (CHA-SCF, SCF/BB) curves, indicating that the correlation contribution (mainly dispersion) obtained from this PT are negative. There is seemingly a contradiction that can be resolved by taking into account that in the MP2-based theories the correlation is calculated

by using the distorted orbitals reflecting charge transfer and, especially, polarization effects while CHA-PT utilizes the undistorted monomer orbitals. Apparently polarized orbitals describe a slightly less compact electron distribution that in turn somewhat reduces the absolute value of the correlation energy. (It is easy to see that the effect of polarization on the correlation cannot appear before the third order of the CHA-PT.)

Conclusion

This article briefly summarizes the *a priori* corrected CHA-PT2 and CHA-MP2 BSSE-free second-order perturbation methods and compares them with the *a posteriori* BB method at the correlated level using several hydrogen bonded model systems. The results show that the BSSE is significant in the interaction energy at the correlated levels, so its removal is very important. The differences of the two perturbational theories discussed

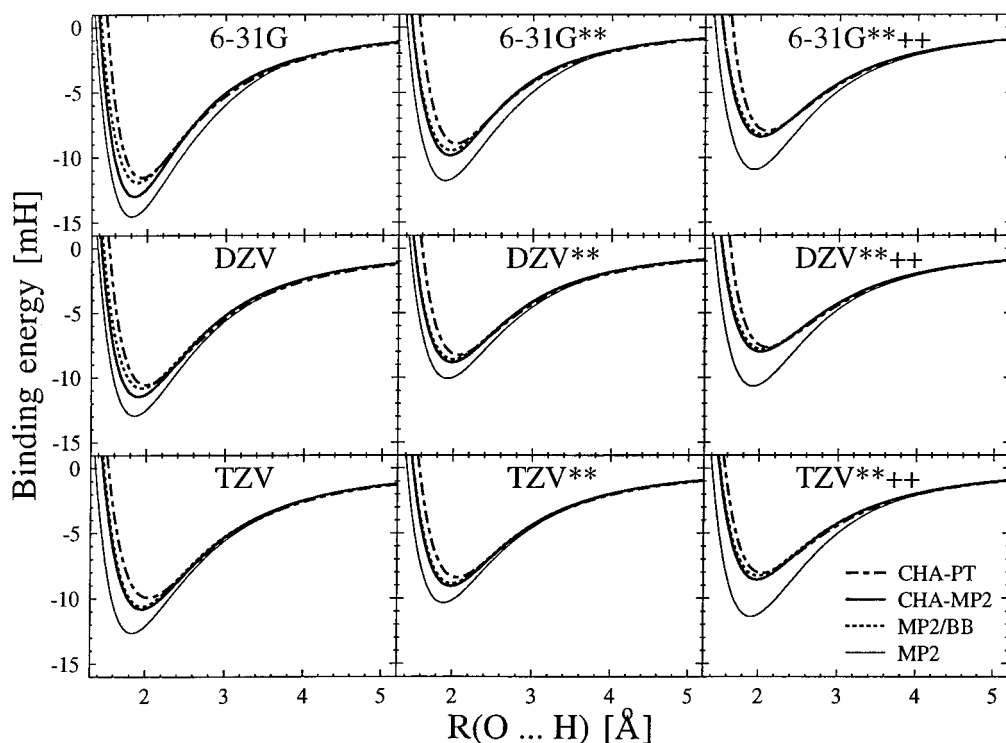


FIGURE 4. Potential curves of the $\text{H}_2\text{O} \cdots \text{HCl}$ system calculated in nine different basis sets as a function of the hydrogen bond length. The coordinates (\AA) are $\text{H}_{\text{A}1}(-0.57087; 0.131797; -0.75669)$, $\text{H}_{\text{A}2}(-0.57087; 0.131797; +0.75669)$, $\text{O}_{\text{A}}(0.0; 0.0; 0.0)$, $\text{H}_{\text{B}}(R; 0.0; 0.0)$, and $\text{Cl}_{\text{B}}(R + 1.2746; 0.0; 0.0)$. The notation of the individual curves is the same as for Figure 1.

are connected solely with the different one electron orbital sets used for building up the unperturbed single determinant wave function.

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